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Interim Report on Non-Flame Hazardous Waste Thermal Destruction

(U.S.) Environmental Protection Agency
Cincinnati, OH

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INTERIM REPORT ON

NON-FLAME HAZARDOUS WASTE THERMAL DESTRUCTION

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The thermal decomposition of toxic organic compounds is being investigated in a laboratory system dedicated to the non-flame mode/zone of the combustion process. The early phase of this study has focused on three compounds: pentachloronitrobenzene (a fungicide), chloroform (a ubiquitous industrial compound) and heptane.

The results of the third compound, heptane, are preliminary to those sought for a mixture of two or more compounds such as chloroform, a toxic substance, and heptane, a combustion process fuel.

The data of this report was collected during the period January - June 1985.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes the results of initial experimentation into non-flame hazardous waste thermal destruction carried out at EPA's Center Hill Thermal Destruction Laboratory in Cincinnati, Ohio.

For further information, please contact the Alternative Technologies Division/Thermal Destruction Branch of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

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INTERIM REPORT ON NON-FLAME HAZARDOUS WASTE THERMAL DESTRUCTION

by

Myron Malanchuk
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ABSTRACT

A laboratory system, identified as the Thermal Decomposition Unit-Gas Chromatograph (TDU-GC), is being used to investigate the impact of key factors of the post-flame zone in the combustion process upon the effluent decomposition products. Thus far, data has been obtained for the thermal treatment of feed samples of pentachloronitrobenzene (PCNB), chloroform and heptane.

Results for the first two compounds have compared favorably with those reported by the University of Dayton Research Institute (UDRI) who developed the TDU-GC.

The results for heptane are preliminary to testing mixtures of chlorinated organic substances and fuel-type hydrocarbons such as heptane.

Indications are that in industrial incineration systems similar thermal treatment of chlorinated organic compounds could generate Products of Incomplete Combustion (PICS) at concentration levels having potential environmental significance.

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INTRODUCTION

In the thermal destruction of hazardous organic waste material, the interactions of the gaseous components in the post-flame or the non-flame zone of the combustion process make an important contribution to the overall results. The thermal decomposition in those zones can range from simple pyrolysis in an oxygen-deficient atmosphere as might occur in a boiler, to a thermal-oxidative treatment with a considerable excess of oxygen as can occur in a liquid injection incinerator supported by a secondary combustion zone or supply of air.

A laboratory unit, identified as the Thermal Decomposition Unit-Gas Chromatograph (TDU-GC), is being used to investigate key thermal decomposition factors of the post-flame zone, such as time of exposure and temperature, and their impact upon the effluent decomposition products. The TDU-GC was developed at the University of Dayton Research Institute (UDRI) and has been applied by Institute personnel over the past several years to study many different organic compounds (1-6).

The TDU-GC at EPA's Center Hill Facility has been used thus far to investigate pentachloronitrobenzene (PCNB) and also chloroform in order to determine the level of reproducibility as measured by the comparison of these findings to those reported by the UDRI for the same compounds. A satisfactory duplication/reproducibility of results would be reassuring in expediting the investigation of other factors and other levels of the thermal destruction parameters.

EXPERIMENTAL PROCEDURE

A. APPARATUS

The principal equipment used in this study was the Thermal Decomposition Unit-Gas Chromatograph, described in detail in a University of Dayton Research Institute report (1).

A brief summary of its construction and operation follows.

The TDU-GC system consists of two basic units, (1) the thermal reactor, for exposing the organic component(s) in the feed to an elevated temperature and (2) the analyzer, consisting of a gas chromatograph for separating the components in the effluent sample drawn from the reactor. These units are emphasized in the basic schematic system, Figure 1.

1. The thermal reactor incorporates a capillary quartz tube within a furnace with three heating zones that are independently controlled to produce temperatures up to 1150°C in the central zone.

A tubular quartz extension at the entrance of the furnace transfers the feed gas from the larger bore sample insertion chamber. That chamber is fitted with any one of several probes adapted to handle gas, liquid, or solid samples. The liquid and solid samples are converted to the

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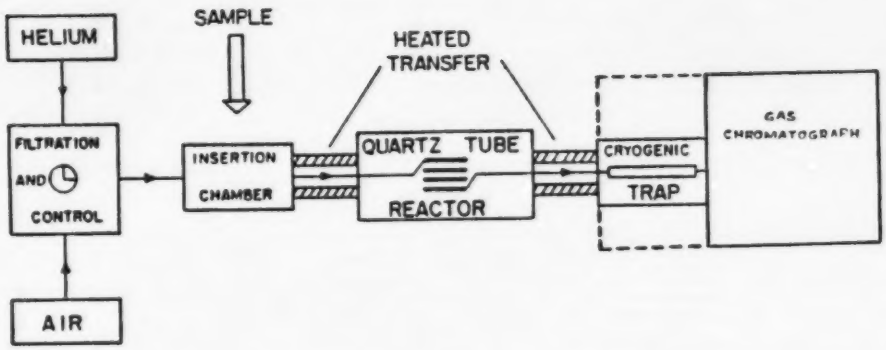

Figure 1. Basic Schematic of TDU-GC System

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vapor phase at elevated temperatures provided by a heating jacket. The vapor is conveyed to the reactor by a controlled flow of carrier gas which is selected according to the nature of the atmosphere required in the high-temperature zone of the reactor. According to the temperature and pressure measured in the reactor tube, the carrier gas flow is regulated at the instrument console to result in a precise residence time of the vaporized/gaseous sample in the closely-controlled high-temperature zone.

The gaseous emissions from the reactor pass through a capillary tube into an in-line tubular trap controlled to sub-ambient temperatures as low as -50°C and colder. The trap is located inside the wall of the gas chromatograph (GC) and is a very short (several mm) section of the extension of the GC capillary column into the 30:1 splitter device.

2. The gas chromatograph, Varian 3700, is fitted with a fused silica capillary column leading to a flame ionization detector (FID). Heating the trap transfers, via the 30:1 splitter, the smaller stream of trapped emissions sample to the front end of the capillary column which itself is at the sub-ambient temperature. Upon injection of the sample into the GC, as initiated by the switch on the CDS-111 computer, the temperature program for the capillary column controls the separation of the components of the reactor emissions sample and their ensuing detection and measurement by the FID.

The CDS-111 computer coupled with an Omniscribe recorder provides a means of storing the output from the FID and depicting it in a chromatogram as well as in a tabulation of the various peak areas.

3. Other equipment, critical to the various measurements involved in the operation of the TDU-GC system include:

a. Syringes, of various volumes
b. Soap bubble flowmeter
c. Aneroid barometer
d. Room temperature thermometer
e. Vapor concentration flask, for preparing known gaseous concentrations of volatile organic compounds

B. REAGENTS and SUPPLIES

1. The several compounds tested during the current study were reagent grade material obtained from a commercial supplier or from a quality control laboratory:

a. Pentachloronitrobenzene (PCNB), $C_6Cl_5NO_2$ (QAS/EMSL, EPA/RTP)
b. Chloroform, $CHCl_3$ (HPLC Grade/Fisher Scientific C-606)
c. Heptane, C_7H_{16} (Distilled in glass/Burdick and Jackson AA-167)

2. In addition, the various organic compounds used in a calibration procedure to confirm GC retention time identities included:

a. Carbon tetrachloride, CCl_4 (Analytical Reagent/Mallinckrodt 4368)
b. Trichloroethylene, C_2HCl_3 (Certified ACS/Fisher T-341)
c. Dichloroethane, $C_2H_4Cl_2$ (Certified ACS/Fisher E-175)
d. Tetrachloroethylene, C_2Cl_4 (Reagent/Baker 9465-1)
e. Hexachloroethane, C_2Cl_6 (Kodak 144)
f. Pentachloroethane, C_2HCl_5 (minimum 96% purity/Ultra Scientific RHH-18)
g. Hexachlorobenzene, C_6Cl_6 (Ultra Scientific CH-150)

3. Cylinder gases for the transfer of the test gas/vapor through the reactor and/or the GC and for the operation of the FID were:

a. Compressed air (Hydrocarbon free/Linde)
b. Helium (High purity/U.S. Bu.Mines)
c. Hydrogen (Zero grade/Matheson)
d. Nitrogen (Zero grade/Linde)

C. SAMPLE FEED

The Principal Organic Hazardous Constituent (POHC) material under investigation was introduced into the insertion chamber as a (1) gas, (2) liquid, or (3) solid.

1. The more volatile, low molecular weight compounds were generally fed to the TDU-GC system in vapor form. For example, a calculated amount of liquid chloroform was delivered from a syringe into a closed 1-liter flask containing air at atmospheric pressure to produce a concentration of 1.00 ug chloroform per 10 ul of the flask air. Then an appropriate quantity of that vapor preparation (10-100 ul) was drawn into a syringe for injection into the TDU-GC insertion chamber.

2. For various organic liquids, nanoliter quantities (10-100 nl) were injected directly into the insertion chamber and vaporized by a programmed temperature increase for transfer by the carrier gas into the thermal reactor.

3. Organic solids were weighed out on a microbalance and then dissolved in such solvents as cyclohexane or methanol to produce the required concentrations. An aliquot, perhaps 1-10 ul of the solution, was drawn into a syringe and then carefully ejected onto the end of the "solids" probe. Evaporation of the solvent left a residue of the organic solid on the tip of the probe which was then expeditiously fitted to the insertion chamber. A programmed temperature elevation of the chamber transformed the solid residues to the vapor state for transfer into the thermal reactor by the carrier gas.

D. TEST RUN

The conduction of a test run is fully detailed in the UDRI report (1).

Initially, the parameters of atmosphere type, temperature level in the thermal reactor and mean residence time are selected and the necessary

steps taken to set those conditions. The temperature selected is adjusted by the controls on the furnace. A source of the required gas is regulated by the instrumentation console control (valve switch and flow control) to provide the necessary flow rate for maintaining the selected residence time of the test gas sample in the high-temperature zone of the furnace. The effluent collection trap in the wall of the GC is cooled to the sub-ambient temperature selected as the starting point for the GC analysis program. The sample is then introduced into the insertion chamber where it is vaporized/mixed with the carrier gas. There follows a continuous transfer of the test sample into the thermal reactor during the period of the temperature rise programmed for that insertion chamber. The effluent products from the thermal reactor are collected in the cold trap. With the switching of carrier gas to helium, the GC analysis is initiated by pressing the injection switch on the CDS-111 computer simultaneously with the start button of the GC temperature programmer. A chromatogram of the product components as well as a tabulation of the peaks (retention times and areas) are obtained with the conclusion of the GC analytical run.

Each test run as described above yields a single point on the thermal decomposition plot (quantity of compound in the effluent vs. temperature of the thermal reactor, with the residence time kept constant) for the POHC material. Corresponding single points for each Product of Incomplete Combustion (PIC) material formed during the thermal treatment run are simultaneously obtained. Runs made over a series of temperatures can produce a thermal decomposition profile of the POHC and formation-decomposition profiles for various PICs, within the temperature limits investigated.

Because of the integrated arrangement of the thermal reactor and the gas chromatograph, calibration runs with known standards at a non-decomposing temperature in the reactor, such as 300°C, are needed in order to identify the PICs produced during a regular run on a POHC substance.

RESULTS

Three series of runs have been completed with the TDU-GC operated as briefly described in the previous discussion. Investigated were (1) pentachloronitrobenzene as a single component feed, (2) chloroform, also as a single component feed, and (3) chloroform in solution with "fuel" heptane constituting the bulk of the organic feed.

1. Pentachloronitrobenzene (PCNB), $C_6Cl_5NO_2$.

The treatment of this POHC material was as follows.

The PCNB originally was prepared in a near-saturated solution in cyclohexane and 2-4 ul of that liquid syringed onto the end of the "solids" probe. After about ten seconds time for evaporation of the cyclohexane, the probe with its film deposit of PCNB was secured to the insertion chamber which then was heated to 300°C at a rate of 25°C/min. The

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resulting vapor was carried by a stream of air through the reactor at a flow rate calculated to allow a mean residence time of 2.00 seconds in the high-temperature zone. The cold trap, set for -25°C, was then heated in the ensuing GC temperature program to yield a chromatogram of individual component peaks as well as a tape record of peak times and area counts and area count percentages of the cumulative count.

The thermal treatment temperatures ranged from 471°C to 571°C that covered a span that had been shown in a previous report (2) to encompass the temperature decomposition profile for that compound. Since the parent compound, pentachloronitrobenzene, was already totally decomposed (>99.99% DE, Destruction Efficiency) at the temperature of 571°C, no higher temperatures were investigated.

The results of the GC analysis are presented in Figure 2 as a plot of reactor effluent "concentrations" vs. exposure temperature. Such concentration is accurately (directly) indicated in curve A which shows the increase in decomposition of the POHC material, the feed pentachloronitrobenzene, with increasing temperature. Curves B, C, and D present the concentrations for the more abundant PICs that were produced in the thermal treatment process. Since component B was later identified as hexachlorobenzene (HCB), a known amount of reagent HCB was introduced as a feed to the TDU-GC system in a separate run to resolve the FID response of the gas chromatograph to that compound. That response was then used to more accurately convert the peak area values (counts recorded on the CDS-111 computer tape) to true concentration values. Since components C and D remained unknown, their peak area values have been presented as though they were directly related to PCNB concentrations, i.e. that each count for those peaks was given the same weight as each count for the PCNB in calculating concentration values.

2. Chloroform, $CHCl_3$

In order to evaluate the TDU-GC system for handling a lower molecular weight, more volatile type organic compound, chloroform was tested as a POHC material.

In one series of runs, chloroform was used in vapor form at a concentration of 1 µg chloroform per 10 µl air. When a 10 ul sample of that chloroform-spiked air was directly injected into the carrier gas stream of the insertion chamber, the subsequent GC analysis of the effluent from the reactor set at a low temperature produced only a tiny blip on the chromatogram for that quantity of chloroform. Subsequent samples of 50 ul (5 ug chloroform) and 100 µl (10 µg chloroform) of the vapor resulted in far more substantial peaks which, nevertheless, were too small for a decomposition study; the FID detector was not very sensitive to chloroform.

In a later series, much larger amounts of chloroform were introduced into the insertion chamber in quantities of 0.10 µl (~150 ug chloroform) and 0.20 µl (~300 µg chloroform) of the pure liquid phase. Like the vapor samples in the earlier series, the liquid samples were injected through a septum directly into the carrier gas (air) stream in a confined region

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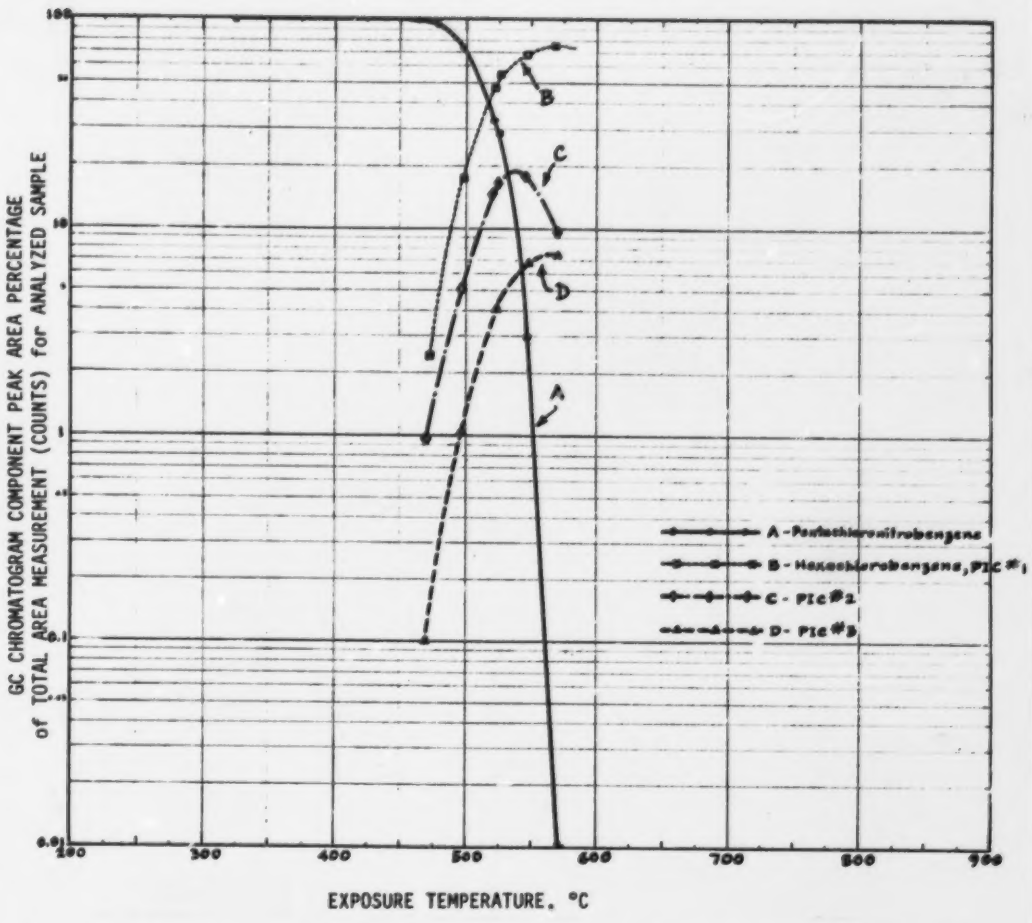

Figure 2. Thermal Treatment of Pentachloronitrobenzene, PCNB ($\bar{\tau}_r$ = 2.0 sec)

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where a plug of quartz wool helped to disperse the injected liquid for effective vaporization. The insertion chamber was programmed to heat up to 125°C at a rate of 10°C/min. Residence time in the high-temperature zone of the reactor was controlled at 2.00 seconds through adjustment of the carrier gas flow. The cold trap for the effluent gas was cooled to -50°C as the starting point for the GC analysis program. The usual GC chromatogram and tape record (CDS-111) of peak times and area counts and percentages were obtained from each run.

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The results from the series of runs using liquid chloroform feed are presented in the decomposition profile seen in Figure 3. The increased decomposition of the chloroform with increasing temperature in the thermal reactor produced major quantities of several PICs. Each of the PICs shown in Figure 3 (hexachloroethane/C_2Cl_6, tetrachloroethylene/C_2Cl_4, and carbon tetrachloride/CCl_4) was identified by retention time checks with the corresponding component introduced individually as the feed in subsequent calibration runs. Minor quantities of other PIC compounds were observed. The highest reactor temperature investigated was 625°C, at which level essentially total destruction (>99.99% DE) of the POHC (chloroform) had occurred.

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Unlike the series for pentachloronitrobenzene, the identification of the major PICs in the chloroform runs facilitated the execution of calibration runs for each of the PICs shown in Figure 3 and thereby permitted more accurate representation of those PIC concentrations in the plot.

3. Chloroform, $CHCl_3$, in heptane, C_7H_{16}

In order to relate more directly to actual conditions of the incineration of chlorinated compounds, chloroform as one of several organic compounds that might be found in a feed mixture, was selected for mixture (solution) in "fuel" heptane to undergo thermal decomposition treatment.

As a first step, heptane alone was investigated at various temperatures to characterize its decomposition, Figure 4. The high temperature of 675°C was considered adequate to bracket the high for "total" chloroform decomposition, namely the 625°C observed in Figure 3. Then, three weight percent of chloroform was added to heptane to determine the effects of the presence of the heptane upon the decomposition profile of the chloroform. The feed, whether pure heptane or chloroform-spiked heptane, was introduced into the insertion chamber as a liquid.

The chromatogram for a sample of heptane that was exposed to a low, non-decomposing temperature level showed a very considerable number of "pollutant" peaks throughout the temperature program range of the GC analysis. Many of these peaks persisted even at higher temperatures where heptane began to decompose.

Subsequent runs for the three weight percent of chloroform in heptane yielded chromatograms in which chloroform and its decomposition products were completely masked by the heptane-source components.

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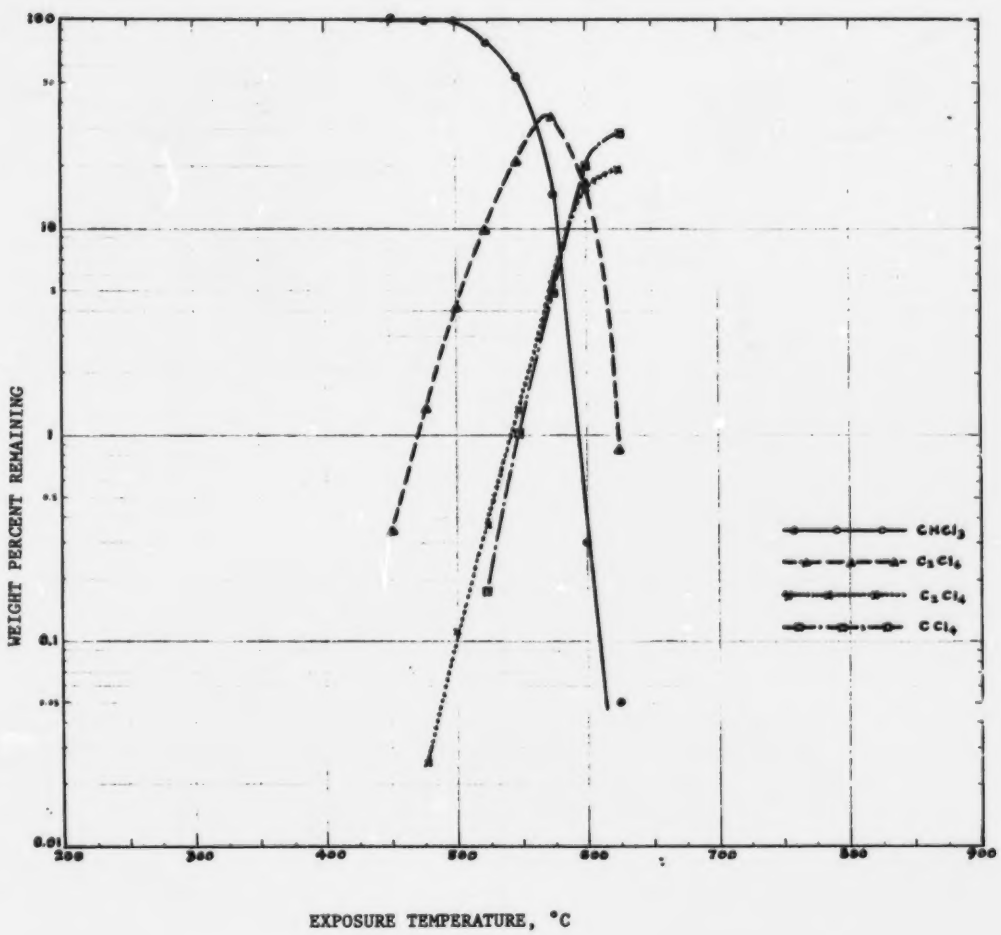

Figure 3. Thermal Treatment of Chloroform ($\bar{t}_T$ = 2.0 sec)

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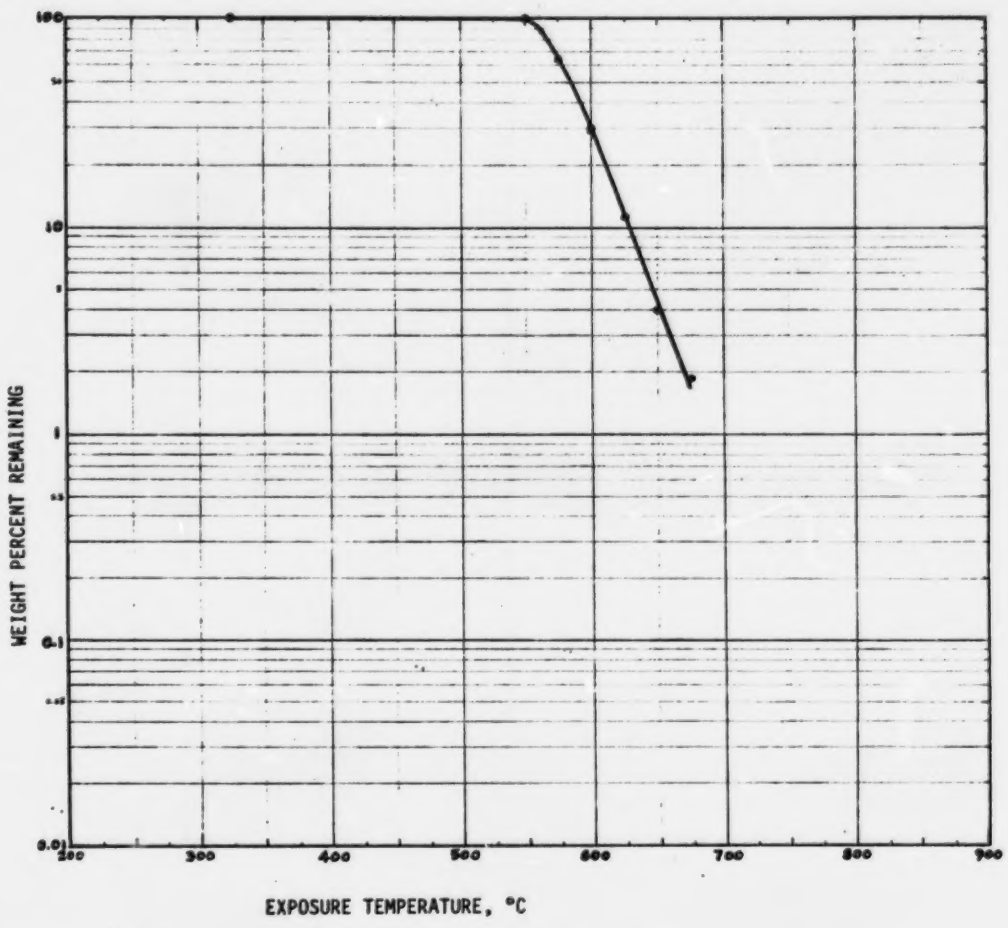

Figure 4. Thermal Treatment of Heptane ($\bar{t}_r$ = 2.0 sec)

DISCUSSION

These initial runs, both with the (1) pentachloronitrobenzene and with the (2) chloroform, were made primarily to check the reproducibility of results when compared to those obtained in the earlier work (2,3) performed on such compounds at the University of Dayton Research Institute (UDRI).

1. Pentachloronitrobenzene (PCNB)

In their report on pentachloronitrobenzene, UDRI presented the results for PCNB and its principal PIC compound, identified as hexachlorobenzene (HCB), as shown in Figure 5.

The results from the present study show a decomposition curve for PCNB that closely matches that reported by UDRI for similar test conditions and that is illustrated by comparing Figure 2 with Figure 5. PIC compounds B, C, and D which appeared in abundant quantities, are also shown, with B identified as hexachlorobenzene and C and D remaining unknown at this time. The hexachlorobenzene formation/decomposition profile, curve B, also closely matches that reported by UDRI.

2. Chloroform

UDRI presented results from their early work with chloroform in the plot of Figure 6 which shows three PICs which were not identified in this early work.

The results of the present study show a deocmposition profile for the feed material, chloroform, that is quite similar to that shown in the UDRI graph. Also the curves for the PICs are generally similar to each other both in shape (rate of change in concentration with temperature) and in relation to the temperature levels. The three PICs shown in the plot for the current work have been identified, as noted in Figure 3.

It is evident, from the chlorine-saturated state of each of the PIC molecules (CCl_4, C_2Cl_4, C_2Cl_6) identified in major concentrations, that the hydrogen atom present in the parent chloroform molecule is being thoroughly eliminated from the organic product species.

It has been suggested that the initial step in chloroform decomposition involves the direct loss of HCl with the formation of the intermediate bi-radical dichlorocarbene (7):

$$CHCl_3 \xrightarrow{\Delta} : CCl_2 + HCl$$

followed by the reaction of that radical with chloroform to form pentachloroethane:

$$:CCl_2 + CHCl_3 \longrightarrow C_2HCl_5$$

UDRI reported that chloroform and pentachloroethane are of comparable stability, i.e., that both these compounds had similar decomposition

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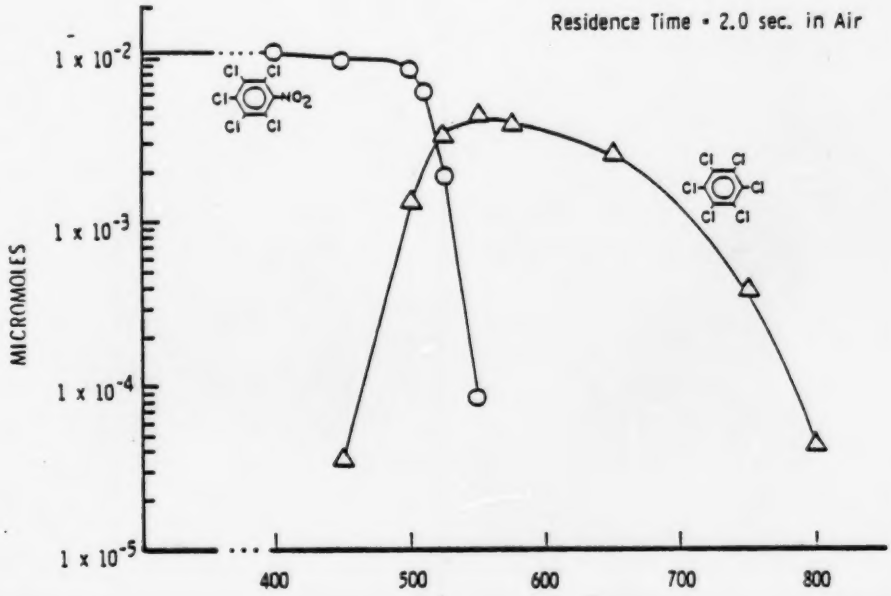

Figure 5. Thermal Decomposition Profile of Pentachloronitrobenzene

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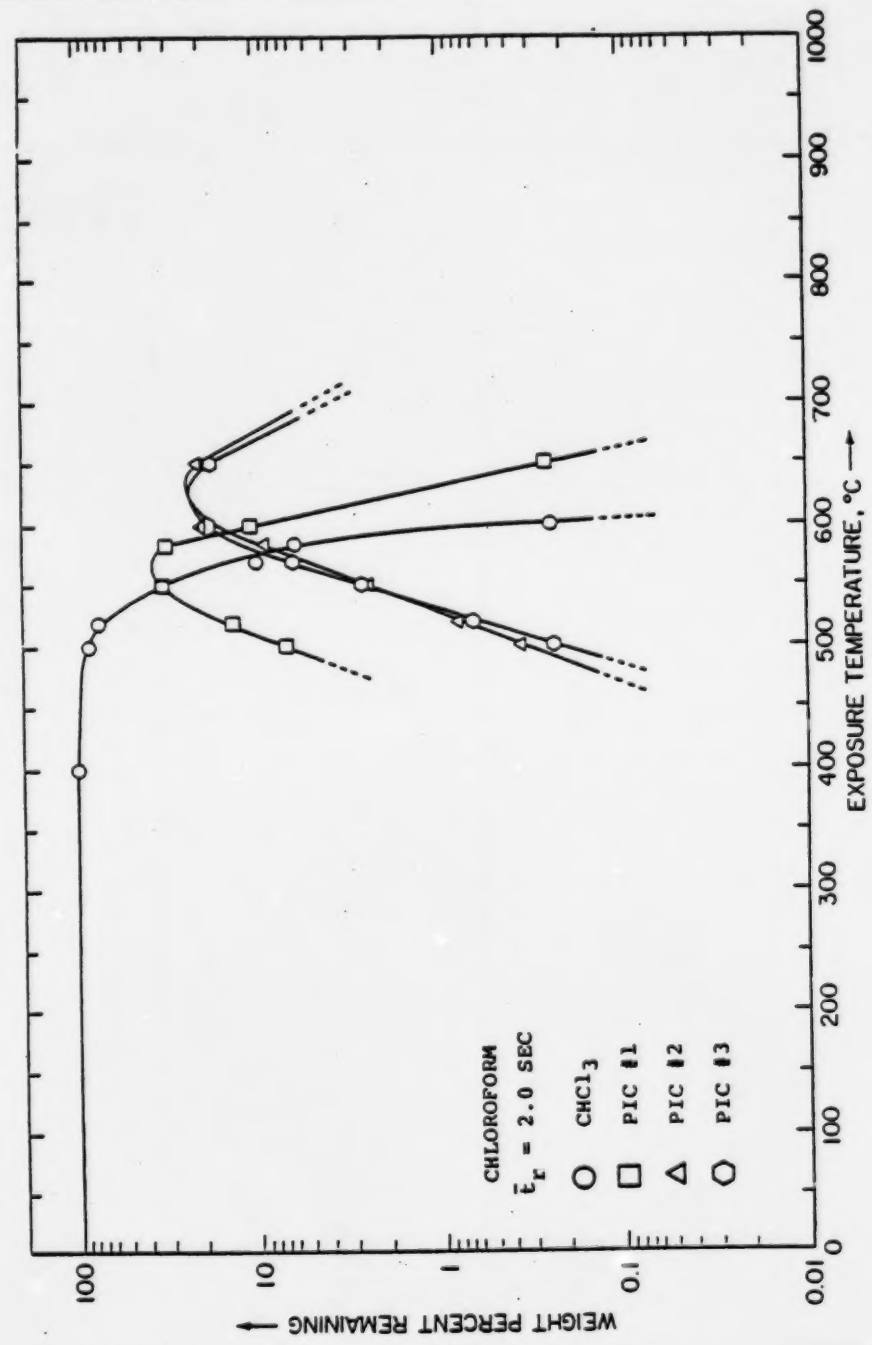

Figure 6. Thermal Decomposition Profile of Chloroform

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profiles within the same temperature range (7).

Under the conditions of the current series of runs, the presence of pentachloroethane was not detected/observed at all, not even in the initial stages of chloroform decomposition. If pentachloroethane was formed, it must have immediately (within the 2.00 seconds residence time in the high temperature zone) reacted to form other compounds, such as tetrachloroethylene, that indeed were detected in significant quantities. Most likely, a decomposition mechanism different from that indicated above (formation of the dichlorocarbene) resulted in the selective removal of the hydrogen atom of the chloroform molecule from further interaction and incorporation in the chlorinated compounds detected in the emissions. Probably, this result was due to the high oxygen/organic-compound ratio prevailing in the current study conditions, with molecular oxygen reacting with and eliminating the hydrogen.

The same values that were used to develop the plots for the four compounds in Figure 3 were also used in Figure 7. Figure 7 presents the results of the thermal treatment of chloroform on an arithmetic (rectangular) scale instead of the semilog scale of Figure 3. The 4-cycle log scale of Figure 3 spans the four decades of concentration of compound that focus on the 99.99% DRE (Destruction and Removal Efficiency) limit factor. Figure 7, on the other hand, clearly shows the comparative amounts of compounds present in the emissions from the thermal reactor.

The curves of Figure 7 readily indicate the relative amounts of potentially toxic PICs being evolved from the decomposition of the parent compound chloroform. The health effects investigator, for example, can perhaps more easily grasp the import of the thermal reaction process from such a typical, standard, graphical display of the test results.

It is evident from Figure 7 that the concentration of the hexachloroethane (C_2Cl_6) has peaked at a temperature (570°C) where the tetrachloroethylene (C_2Cl_4) and carbon tetrachloride (CCl_4) are only beginning to form. The simultaneous "growth" of the latter two compounds suggests that a common mechanism producing those two compounds at the same time may be in effect at those temperature levels.

3. Chloroform in heptane

In light of the effective masking of the GC peaks for chloroform and its products by the heptane source pollutants, work was suspended on this phase of the study until a "cleaner" heptane could be obtained and checked for feasibility of its use in this study phase.

A decomposition profile was, however, obtained for the heptane and is shown in Figure 4. It is evident that decomposition begins at a temperature slightly greater than 550°C. However, the decomposition rate shows up as a substantially straight line plot of moderate slope on the semilog scale so that by 675°C a little more than one percent of the heptane still persists in its presence in the effluent stream from the reactor.

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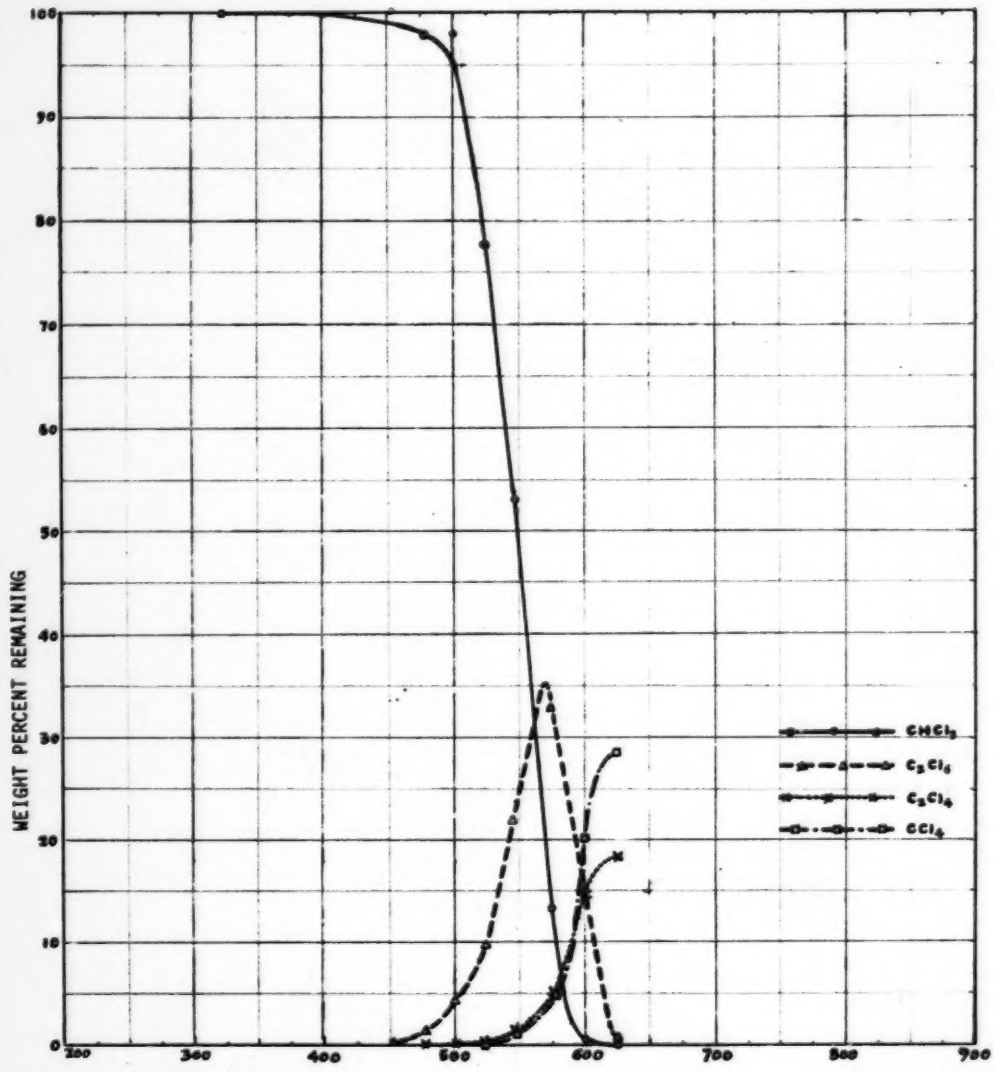

Figure 7. Thermal Treatment of Chloroform ($\bar{t}_r$ = 2.0 sec)

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CONCLUSIONS and SUMMARY

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The Thermal Decomposition Unit-Gas Chromatograph (TDU-GC) system has been used in obtaining thermal decomposition profiles for several organic compounds associated with the incineration of toxic/hazardous organic waste substances.

The system has been used successfully to demonstrate reproducibility of results consistent with the findings of other invesigations, namely those reported for like compounds by the University of Dayton Research Institute in earlier work done by the TDAS (Thermal Decomposition Analytical System) and/or the TDU-GC system.

However, the experience with heptane as a component in the feed to the TDU-GC suggests that there will be great difficulty in properly assessing mixtures of organic compounds exposed to the thermal treatment process. For accurate measurement of effects of feed composition, great care will have to be taken to limit mixtures to a very few, perhaps only two, compounds that are individually "clean" in any GC analysis.

For more fully characterizing the thermal reactor emissions with respect to PICs formed in the thermal treatment process, more extensive procedures involving additional instrumentation is needed to identify and quantify PIC compounds. A Mass Selective Detector (MSD) dedicated to the TDU-GC system is the instrument of choice, both for accuracy of determinations and for volume of work that can be expedited. An alternative scheme for analyzing the emissions requires trapping the by-pass volume of effluent at the splitter ahead of the GC capillary column onto an adsorbent and then analyzing the adsorbed sample by an "external" GC-MS unit to identify PIC compounds. This latter procedure offers the opportunity for identifying individual PIC compounds that otherwise might remain unknown. However, the various additional handling steps and transfer(s) of samples present a serious obstacle to accurate quantification. Practical limits to the load of samples that can be handled in this way would require great selectivity in the kind and number of samples that could be designated for analysis.

Early in the study, an experimental design treatment (8) through statistical evaluation of parametric projections and anticipated results was proffered as a means to streamline the investigative program. Unfortunately, various factors not able to be controlled and unknowns not anticipated at the time nullified this effort. Some of these were singularities of the "art" of performing the experimental runs that cannot be statistically accountable. For example, the use of a mini-injector syringe needed for some samples required a trial-and-error approach of timing the injection and of spotting the delivery tip at a certain depth in the insertion chamber, etc., in order to arrive at a consistent procedure for yielding acceptably reproducible results - this resolution before a planned series of runs at various temperatures might be considered. Another problem involved vapor samples of chloroform that yielded too small a quantity of the organic compound(s) in the emissions

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for satisfactory quantification of that less detector-sensitive compound; liquid samples were substituted for resolving that particular part of the study under the test conditions prevailing at that time. Of course, various equipment breakdowns not only stopped the course of investigation but even required back-tracking sometimes to re-establish a controlled set of operating conditions. The active interjection of various unknowns into the study procedure make experimental design ineffective in such a non-routine environment of investigation.

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